TG/DTG/MS COUPLED METHODS FOR THERMAL ANALYSIS OF NEW MATERIALS FOR OPTICAL FIBER TECHNOLOGY

Małgorzata Gil[1], Beata Podkościelna[2], Paweł Mergo[1]

[1]Laboratory of Optical Fibre Technology, Maria Curie-Skłodowska University, Lublin, Poland

[2]Department of Polymer Chemistry, Maria Curie-Skłodowska University, Lublin, Poland

Abstract

In this study bulk polymerization of methacrylic derivative of thiophenol (PSM) with commercial monomers styrene (St) and methyl methacrylate (MMA) was presented. This monomers had been chosen because of their good thermal and optical properties, which make them useful in optical fibres technology. Copolymerization MMA or St with PSM in glass form, with different weight ratio of monomers (1:10, 1:20; MMA or St : PSM) was performed. As a initiator α,α'-azoiso-bis-butyronitrile (AIBN) was used. This process was carried out in water bath at 60 °C for 2 h and 90 °C for 12 h. As an analytical method coupled TG/DTG/QMS was used.

Key words: *thiophenol, copolymers, thermal properties, optical fibers*

1. INTRODUCTION

Typically optical fibers are made of glass, but in recent years, there can be observe an increased interest in polymer optical fibers (POFs). This relates to the differences in properties between them and the silica glass optical fibers. The fibers made of glass, mainly for telecommunication applications, have a relatively small diameter, usually 125μm, to allow them to be flexible despite of their inherent brittleness. This causes many problems during their connection. Polymer optical fibers can be produced with relatively large dimensions, which greatly simplify their connection. Unfortunately, polymer optical fibers have a higher attenuation, due to increased scattering. But still owing to its unique features such as low processing temperatures and great compatibility, which allow for the doping of a wide range of organic materials, makes polymer optical fibers the object of great interest. Due to the much lower Young's Modulus and much higher thermos-optic coefficient POF may acquire special functionalities for many applications in photonics, material science, medicine and optical sensing [1-4].

The main problem in polymer optical fiber technology is the purity of the materials. Even a small amount of impurities can significantly decrease the transmission properties of the final product. This is why before the use all substances have to be purified. Another problem, which relates to the mentioned, are the thermal properties of the polymer matrix. To be able to draw a fiber from polymer preform, the polymer needs to have good thermal stability. For pol (methyl mathacrylate) and styrene this temperature is about 200 – 220 °C. Our studies showed [5] that after adding a dopant to the matrix, the temperature properties are changing. To increase the thermal resistance of the studied polymers and not to have to add another compound (which could cost a transmission lowering) we decided to add to the composition methacrylic derivative of thiophenol, which is well known also as a chain transfer agent [6-8].

This article presents the thermal and spectroscopic studies of copolymers MMA or St with new synthesized methacrylic derivative of thiophenol (PSM). The degree of usefulness of the received materials as optical materials has been studied using the coupled thermal and spectroscopic methods. Benefits resulting from the coupling of these methods rely on the fact that they give complementary data on the polymer molecule, which is very effective in the identification of unknown polymer materials. Moreover, chemical characterization of materials particularly for use in the manufacturing of optical fibers and also analysis of the chemical composition of the gases emitted from the heated sample affecting the properties of the produced fibers - definition of the causes of heterogeneity in fiber preforms. The analysis can get information on determination of the thermal processing of materials for optical applications and also determine how to prevent thermal decomposition of the samples.

2. EXPERIMENTAL

Methacrylic derivative of thiophenol was obtained according to procedure presented in Ref. 9 This compound was synthesized in the reaction thiophenol with methacryloyl chloride in ice bath (0-5 °C). Styrene was from Fluka AG (Buchs Switzerland). α,α'-Azoisobisbutyronitrile (AIBN) was obtained from Merck (Darmstadt, Germany). All chemicals were used as received.

Bulk polymerization of methacrylic derivative of thiophenol (PSM) with commercial monomer: styrene (St) is presented. Copolymerization St with PSM in glass form, with different weight ratio of monomers (1:10, 1:20) styrene: PSM was performed. 1 % of α,α'-Azoiso-bis-butyronitrile was used. This process was carried out in water bath at 60 °C for 2 h and 90 °C for 12 h. Homopolymers of styrene and methyl methacrylate were obtained in the same conditions

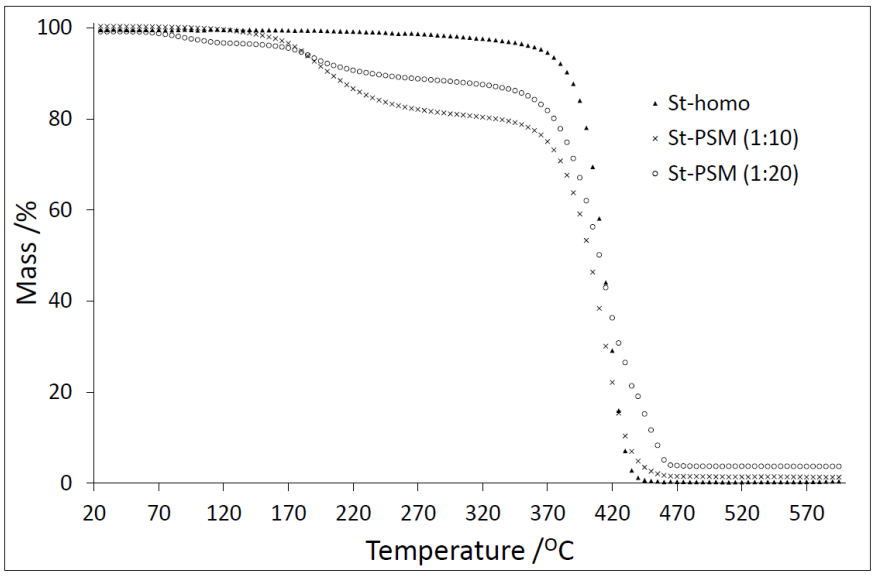
3. RESULTS AND DISCUSSION

Thermal analysis was carried out on a STA 449 Jupiter F1, Netzsch (Selb, Germany) under the following operational conditions: heating rate 10ºC min^{-1}, a dynamic atmosphere of helium (50ml min^{-1}) in the temperature range of 20–600ºC, sample mass of about 5 mg, sensor thermocouple type S TG-DSC. As a reference, empty Al crucible was used. The identification of gas composition coming out during depolymerization and decomposition process were detected and analyzed by quadrupole mass spectrometer QMS 403C Aëolos (Germany) coupling on-line to STA instrument. The mass spectrometer was connected on-line to STA instrument by quartz capillary heated to 300ºC. The QMS was operated with an electron impact ionizer with energy 70eV. The measurements performed in scan mode for *m/z*, where *m* is the mass of molecule and *z* is a charge of the molecule in electron charge units in the range from 10 to 100 amu allowed to identify all possible volatile particles produced during the decomposition.

3.1 Thermal properties of copolymers

Based on thermogravimetric data (Fig. 1) it was possible to determine the mass loss at which the samples decomposition or depolymerization begins (T_{onset} is the temperature at which continuous mass loss is recorded and T_{offset} is the temperature at which decomposition is finished) and the mass loss at the temperature (220 ºC) at which polymer optical fibers, made by PMMA or St, are sufficiently malleable for drawing processes. These three parameters are crucial in optical fibers technology.

a)



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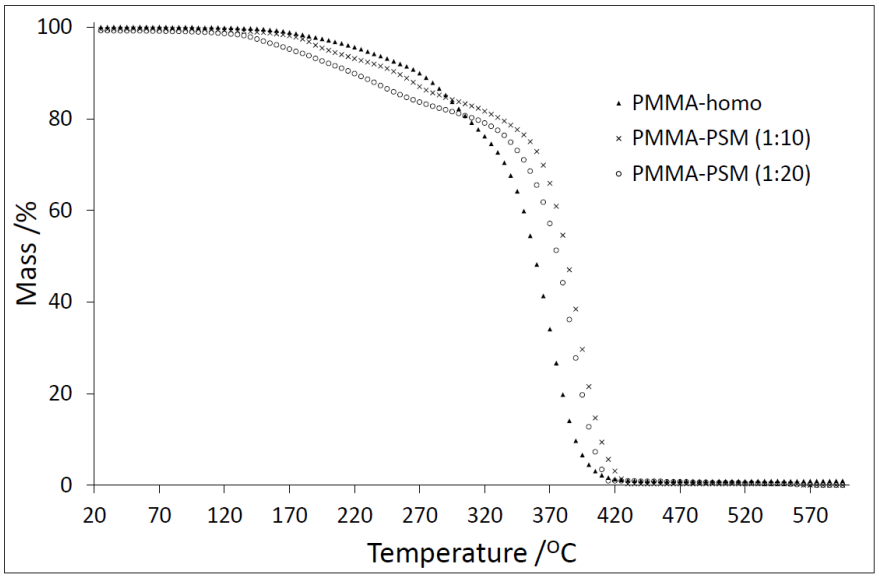

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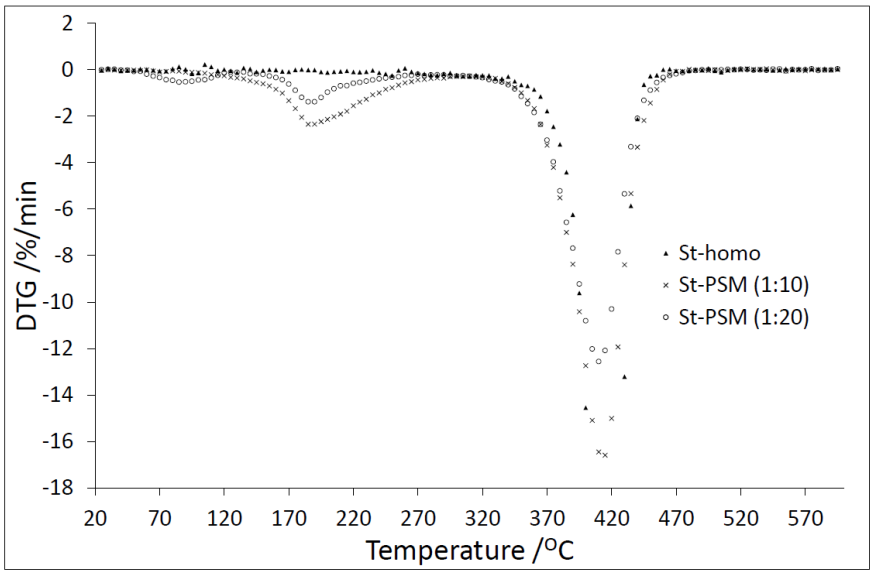

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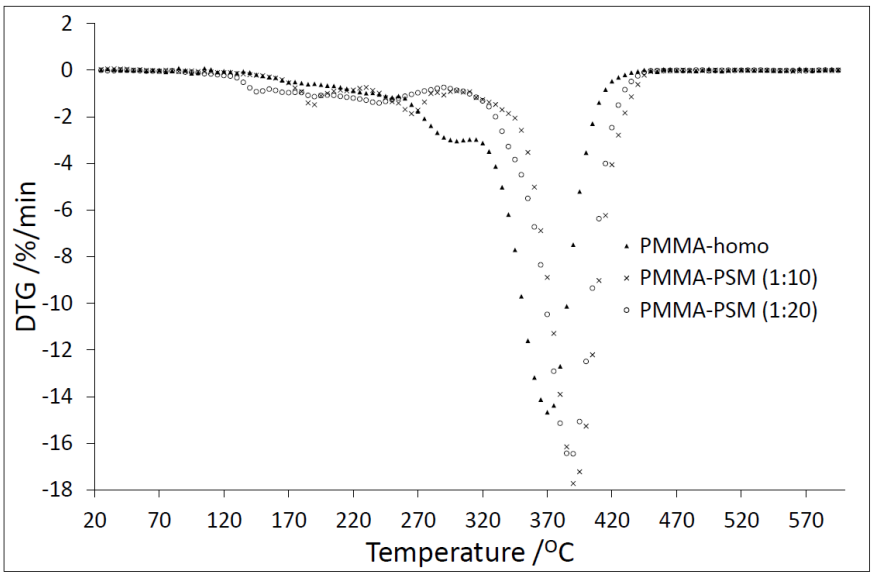


Fig. 1. TG (a, b) and DTG (c,d) curves for all tested materials.

All the thermoanalytical results were summarized in Table 1.

Table 1. The analysis of the TG and DTG curves of the St-homo, MMA-homo and St-PSM, MMA-PSM (1:20; 1:10).

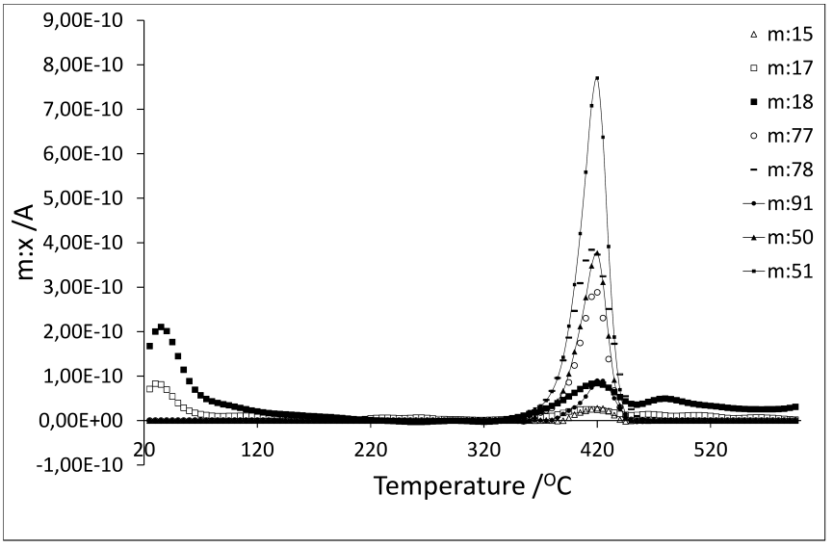
Polymer	Mass loss at 220 ºC /wt.%	DTG $_{max}$ /ºC	T_{onset}	T_{offset}	Residual mass /wt.%
St-homo	0.8	415	373	445	0
St-PSM (1:20)	9.5	190/410	368	445	3.7
St-PSM (1:10)	13.3	190/415	370	450	1.3
MMA-homo	4.3	250/295/370	275	412	0
MMA-PSM (1:20)	10.1	150/240/385	330	431	0
MMA-PSM (1:10)	6.8	190/265/390	360	439	0

Analysis of the TG/DTG data leads to the conclusion that the synthesized copolymers are characterized by good thermal resistance. The maximum decomposition temperature (DTG_{max}) for homopolymer of styrene is observed at 415°C and for copolymers with PSM (1:20, 1:10) at 410.4°C and 415°C, respectively. There can be observe additional DTG_{max} at 190°C for both St-copolymers, which are related to the thermal decompositon process, confirmed by MS-spectroscopy (Fig.2).

As shown, the onset temperature of decomposition is very similar to all St samples, and reaches about 370°C and the same is observe for T_{offset} temperatures, which for al St samples reaches about 445°C. Much interesting is the samples thermal behavior at 220 ºC. Looking at the mass loss at this temperature it can be concluded that by increasing the amount of the dopant the thermal resistant decreases and this is probably caused by increase the aliphatic groups amount. This also confirmed why the residual mass for sample with highest amount of the dopant is lower than for the sample St-PSM (1:20).

By looking at results obtained for MMA samples one can observe that the decomposition is three-step process. The first mass lost is probably caused by water evaporation which is confirmed by MS-spectroscopy (Fig.2), the second and the third are decomposition and depolymerization processes further confirmed by MS analysis. The maximum decomposition is quite similar for all tested MMA samples, but it can be seen that buy increasing the amount of the dopant temperature also increases. The same scheme can be observe for T_{onset} and T_{offset} temperatures. The thermal behavior for MMA-samples is different to St-samples. The highest amount of the dopant improves the thermal resistance. Residual mass for all samples is 0 wt.%.

3.2 Spectroscopic properties of copolymers



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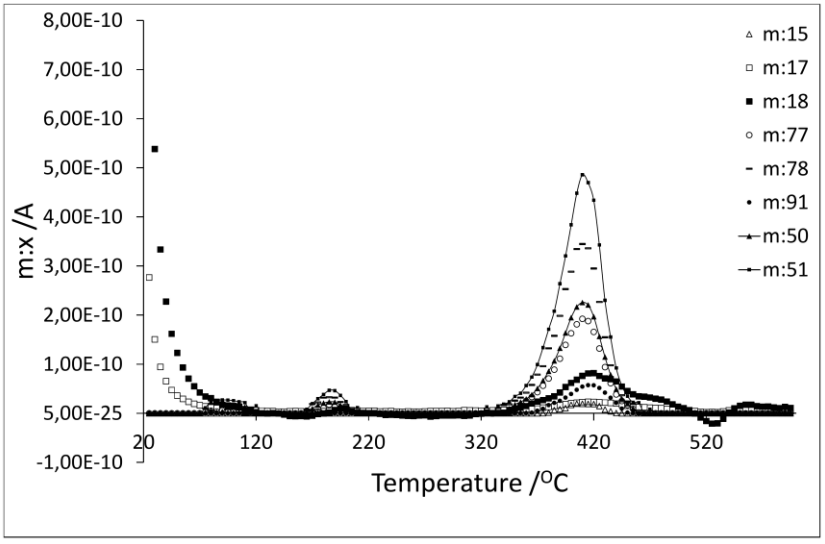

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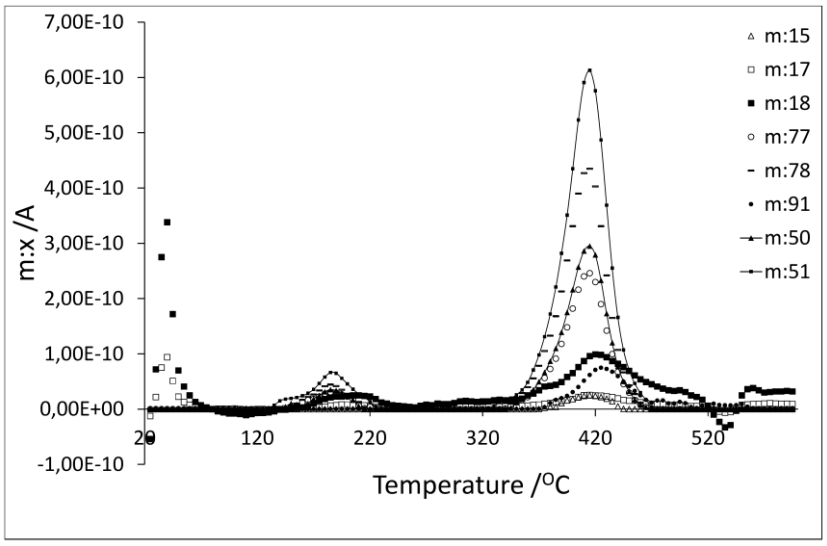

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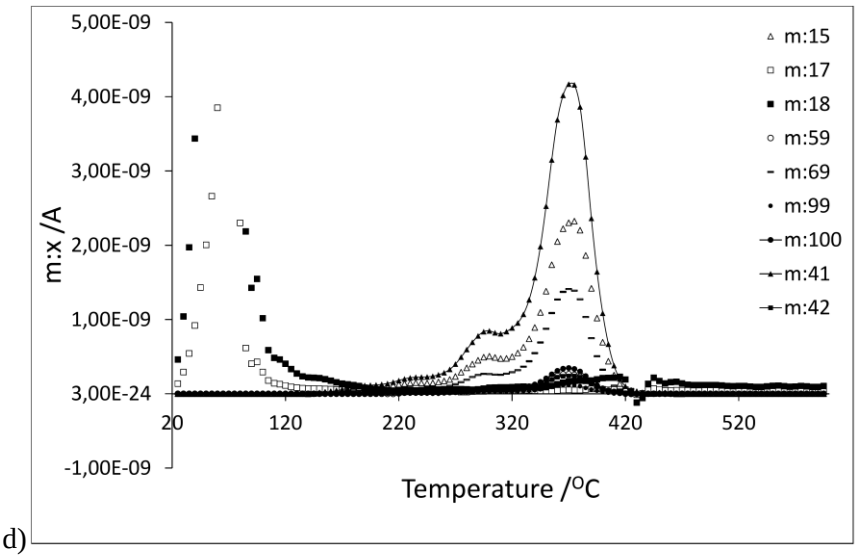

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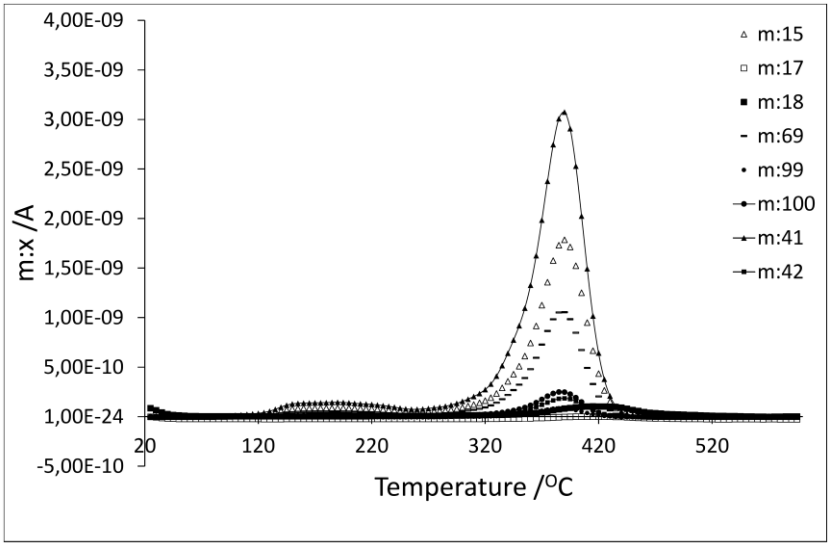

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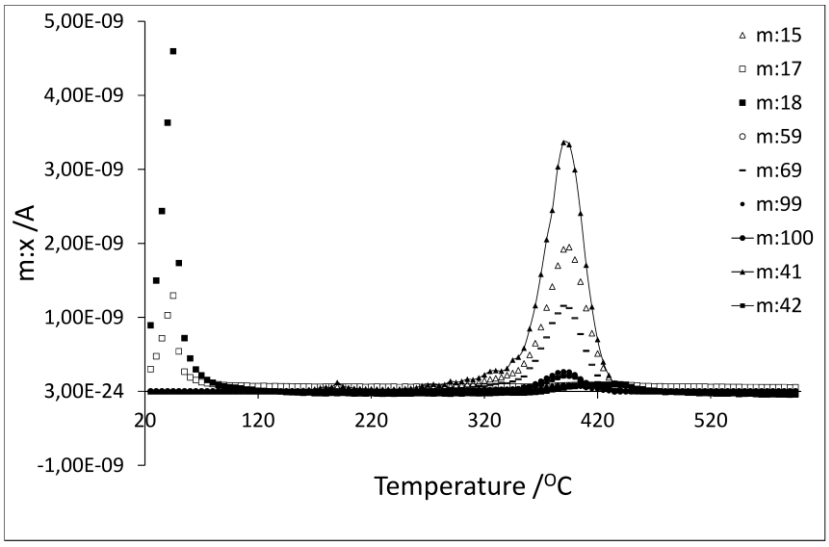

f)

Fig. 2. QMS analysis: a – St-homo, b – St-PSM (1:20), c – St-PSM (1:10), d – MMA-homo, e – MMA-PSM (1:20), f – MMA-PSM (1:10).

As it is visible, QMS analysis (Fig.2) directly confirms the results obtained based on TG/DTG studies. For all tested samples (St and MMA) the first loss mass are related to the water evaporation (m/z = 17, 18). Besides this inorganic gas, the emission of organic volatile products is also detected. Based on ion fragmentation values we can directly confirmed the presence of phenyl group (m/z = 50, 51, 77, 78), benzyl group (m/z = 91) and methyl group (m/z = 15) in St-copolymers which explains the mass loss recorded by TG/DTG analysis before the temperature reaches the decomposition step. The presence of these ions was not observe in St-homo. Based on obtained results it was confirmed that the addition of the dopant decreases the thermal stability of the samples. For samples based on MMA also the first mass loss is related to the water evaporation (m/z = 17, 18) the rest of the mass loss is related to the presence of methyl groups (m/z = 15), ions m/z = 41, 42, 69 are typical for methacrylate derivatives, which contains double bond in their structure (CH_2=$CHCH_2$, CH_2=$CHCH_3$, CH_2=$C(CO)CH_3$) and ion m/z = 59 ($C_3H_3O_2$) which is responsible to the presence of methylene esters. As it can be seen the sample MMA-PSM (1:10) it is the most stable, which confirmed the TG/TGD analysis. It can be observe the presence of water at the beginning of temperature increase but then till the proper decomposition there are any ions detected.

4. CONCLUSIONS

Synthesis of the new bulk copolymers of methacrylic derivative of thiophenol (PSM) with styrene and methyl methacrylate was proposed.

Synthesized copolymers are characterized by good thermal resistance. The maximum decomposition temperature (DTG_{max}) for styrene copolymers is in the range 410.4 - 415°C and for methyl methacrylate copolymers at 370 - 390 °C, respectively. For MMA copolymers the decomposition is three-step process. The thermal behavior for MMA-samples is different to St-samples. The QMS analysis confirmed results obtained from TG/TDG studies. The highest amount of the dopant improves the thermal resistance for MMA samples and decreases for St samples.

REFERENCES

[1] C. Zhang, J. Lin, *Defect-related luminescent materials: synthesis, emission properties and applications*, Chemical Society Reviews 41 (2012) 7938-7961.

[2] D. Webb, K. Kalli, *Polymer fiber Bragg gratings*, in Fiber Bragg Grating Sensors: Recent Advancements, Industrial Applications and Market Exploitation, A. Cusano, A. Cutolo, and J. Albert, Eds. Sharjah (Bentham Science Publishers 2011), pp. 292-312.

[3] G.D. Peng, P.L. Chu, *Polymer optical fiber photosensitivities and highly tunable fiber gratings*, Fiber and Integrated Optics 19 (2000) 277-293.

[4] K. Gąsior, T. Martynkien, G, Wójcik, P. Mergo, W. Urbańczyk, *D-shape polymer optical fibres for surface plasmon resonance sensing*, Opto-electronics Review 24 (2016) 209-215.

[5] M. Gil, B. Podkościelna, B. Gawdzik, A. Bartnicki, W. Podkościelny, G. Demirci, *Synthesis and characterization of vinyl derivatives of naphthalene-2,7-diol as a photoluminescent dopant useful in optical materials*, DOI 10.1515/pac-2016-1002.

[6] C. Henriquez, C. Bueno, E. A. Lissi, M.V. Encinas, *Thiols as chain transfer agents in free radical polymerization in aqueous solution*, Polymer 44 (2003) 5559-5561.

[7] T. Furuncuoglu, I. Ugur, I. Degirmenci, V. Aviyente, *Role of Chain Transfer Agents in Free Radical Polymerization Kinetics*, Macromolecules 43 (2010) 1823-1835.

[8] F. Karasu, N. Arsu, Y. Yagci, *2-Mercapto Thioxanthone as a Chain Transfer Agent in Free-Radical Polymerization: A Versatile Route to Incorporate Thioxanthone Moieties into Polymer Chain-ends*, Journal of Applied Polymer Science 103 (2007) 3766-3770.

[9] B. Podkościelna, K. Fila, M. Grochowicz, Thermal and spectral analysis of copolymers with sulfur groups, Journal Thermal Analysis and Calorimetry (submitted).